



Sedimentological and geochemical characterization of river suspended particulate matter (SPM) sampled by time-integrated mass flux sampler (TIMS) in the Sava River (Croatia)

Mavro Lučić¹ · Irena Jurina¹ · Janez Ščančar² · Nevenka Mikac¹ · Neda Vdović¹

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Abstract

Purpose Suspended particulate matter (SPM) plays a crucial role in the transport of natural and anthropogenic substances. However, obtaining a representative sample and a substantial amount of SPM in rivers, where the flux and quantity of SPM are highly episodic, can be a challenging task. To collect a sufficient quantity of SPM for detailed sedimentological and geochemical analysis, a time-integrated mass flux sampler (TIMS) was used for the sampling in a medium size river (the Sava River, Croatia).

Materials and methods Sampling was conducted in August and October 2014, and February and May 2015 under different discharge conditions. The SPM collected by TIMS was characterized with respect to its particle size distribution (PSD), mineral content, and geochemical composition.

Results and discussion PSD analysis identified silt as a dominant size fraction in all samples except in May 2015 when sand prevailed; subsequent chemical dispersion of samples revealed flocculation as the main factor responsible for the resulting PSD. The mineralogical composition of the SPM was quite constant (quartz, calcite, dolomite, feldspar, illite/muscovite, kaolinite), but the contribution of particular mineral varied depending on the sampling period. In May 2015, unusually high calcite content was determined. Though the dominant source is still uncertain, a portion of calcite is likely detrital in origin. Geochemical analyses of collected material revealed significant anthropogenic input of ecotoxic elements (Ni, As, Cr, Pb, Bi, Cd, Zn, Sb) primarily associated with the fine fraction of the Sava River SPM.

Conclusions A considerable amount of the SPM was collected by TIMS, both during high and low river discharge. Sedimentological analyses of the Sava River SPM suggested the input of material from various sources during different river regimes. Geochemical composition of the SPM followed its sedimentological characteristics—preferential adsorption of trace elements to fine-grained clay mineral particles was documented. Some processes inside TIMS were observed during this investigation—the suspended material captured inside the sampler underwent additional changes. The flocculation of the colloidal material instigated by algal bloom was observed.

Keywords Geochemistry · Suspended matter · The Sava River · Time-integrated sampler · Trace elements

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✉ Neda Vdović
vdovic@irb.hr

¹ Department for Marine and Environmental Research, Ruđer Bošković Institute, Bijenička cesta 54, 10000 Zagreb, Croatia

² Department of Environmental Sciences, Jožef Stefan Institute, Jamova 39, 1000 Ljubljana, Slovenia

1 Introduction

The global contribution of river-derived sediments comprises up to 95% of the material entering the world oceans, and the suspended particulate matter (SPM) accounts for most of the riverine sediment load (Syvitski 2003). In addition, Horowitz (1991) indicated that more than 90% of the flux of trace elements is associated with fine particles transported in suspension, which highlights the importance of the SPM in the transport of many natural and anthropogenic substances.

The SPM is identified as the material having a lower size limit of 0.45 µm in median diameter (d₅₀) (Baalousha et al.

2009). In fine sediment dominated rivers, the upper size limit is not so definite. The literature data report sizes up to 500 μm , predominantly due to the flocculation/aggregation processes in the water column (Droppo et al. 1997; Walling et al. 2000; Woodward and Walling 2007; Bouchez et al. 2011a, b). The flocculated material can account for more than 90% of the total volume of the sediment carried in suspension (Droppo and Ongley 1994) and is characterized by highly complex structures, composed of small inorganic particles, organic matter, and pore water (Droppo 2001, 2005).

Inorganic particles can be the principal component of the river suspended sediment samples, at times comprising more than 70 wt.% (Ongley et al. 1981; Hiller 2001). The composition of inorganic particulate matter predominantly includes primary (quartz, feldspars, and carbonates) and secondary (illite, smectite, chlorite, and kaolinite) mineral phases and amorphous metal oxyhydroxides (Viers et al. 2009). The organic component of the SPM comprises microbial communities and organic particles (e.g., detritus, extracellular polymers, and cellular debris) (Droppo 2001).

Retrieving a representative sample and an ample amount of the SPM is a task hindered by several factors: (1) suspended material fluxes are highly irregular, so sampling activity should be focused on high sediment and contaminant load associated with high discharge periods; (2) adequate sampling equipment is not readily available and sampling can be costly; (3) individually (daily) taken samples may not be representative of material transported during the extended periods; (4) collecting a sufficient mass of suspended sediment for numerous analyses could be a tedious and time-consuming task (Walling 2005; Smith and Owens 2014).

To overcome these impediments, Phillips et al. (2000) designed a time-integrated mass flux sampler (TIMS) for collecting suspended material in small catchments. The sampler was subsequently tested under different environmental/hydrodynamic conditions (Russel et al. 2000; McDonald et al. 2010; Smith and Owens 2014) and proven useful in several studies (Ankers et al. 2003; Ballantine et al. 2008; Martínez-Carreras et al. 2012; Marttila et al. 2013; Massoudieh et al. 2013). In this investigation, TIMS was employed for the SPM sampling in a medium size river, the Sava River.

Previous studies investigating the environmental status of the Sava River primarily focused on water and sediment quality with respect to different organic (Smital et al. 2013) or inorganic pollutants (Oreščanin et al. 2004; Ogrinc et al. 2008; Milačič et al. 2010; Murko et al. 2010; Vidmar et al. 2016). Suspended material was rarely included in those investigations. The only available data report trace elements concentrations in the SPM samples collected on a single occasion along the Sava River watercourse (Ogrinc and Ščančar 2013; Vidmar et al. 2016; Milačič et al. 2017). Considering this scarcity of data, this investigation was undertaken for more thorough sedimentological and geochemical characterization

of the SPM in the Sava River. Particular emphasis was put on a fine-grained fraction as a main carrier of pollutants. This paper presents preliminary results of the SPM characteristics sampled by TIMS at one location over four sampling periods.

2 Materials and methods

2.1 The study area

The Sava River is a transboundary watercourse flowing through Slovenia and Croatia, alongside the northern border of Bosnia and Herzegovina, and finally through Serbia, where it flows into the Danube River at Belgrade (Fig. 1). The river begins at the confluence of the Sava Dolinka and the Sava Bohinjka headstreams in northwestern Slovenia, upstream of the city of Ljubljana (Kanduč et al. 2007). It is 990 km long, with drainage basin covering 97,713 km² of surface area. The Sava River has mountainous, Alpine and Dinaric, characteristics up to Zagreb, where it becomes a typical lowland river (Riđanović 1983). In the years 1961 to 1990, annual rainfall amounts in the Sava river basin was between 800 and 1600 mm with the highest precipitation in the Alpine region of Slovenia (Ogrinc et al. 2008). Annual temperature for entire basin was 9.5 °C (Komatina and Grošelj 2015).

The Sava drainage basin is lithologically heterogeneous, particularly in Slovenia (Buser et al. 1989). Triassic carbonate rocks dominate in the upper watershed (limestone and dolomite) and Pleistocene fluvioglacial sediments near the town of Radovljica. The central part of the Sava basin is composed of Permo-Carbonian clastic sediments, followed by Triassic carbonates and Miocene clastic rocks in the area before the border with Croatia.

In Croatia, the drainage area of the river comprises Pleistocene limestones, marls, and clays interbedded with sand underlying the Quaternary deposits. The Holocene is represented by alluvial sediments deposited by the Sava River and its tributaries (Šimunić and Basch 1975).

The hydrologic characteristics of the Sava River in Croatia are controlled by the rain–snow regime; the highest flows occur in March, caused by snow melting, and in November, due to the autumn rains. The average annual instantaneous discharge at the Zagreb gauging station in the period 1926–2004 was 310 m³ s^{−1}, with minimum and maximum values being 46 and 3126 m³ s^{−1}, respectively (Bonacci and Ljubenkov 2008).

Increasing human activities, such as regulations of the river course, construction of dams, reservoirs, and channels, pumping large quantities of underground water, and uncontrolled exploitation of gravel, are especially pronounced in the upper reaches of the Sava River and are continuously changing the amount of riverine suspended and bedload sediments. This reduction of the material load is affecting the downstream

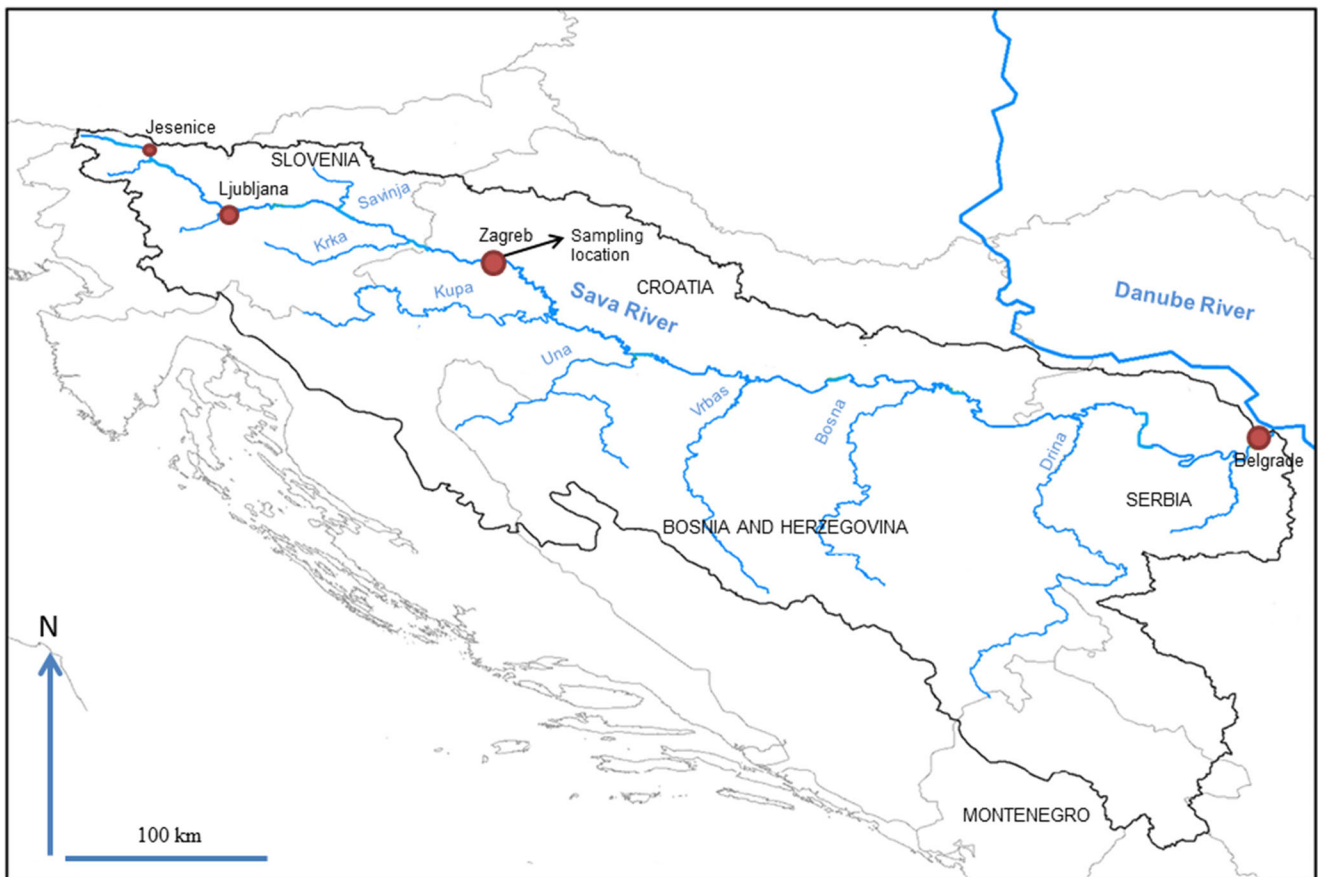


Fig. 1 Sampling location (modified from Globevnik et al. 2004–2007). Gray lines denote country borders, black line is catchment border

river parts, where deepening of the river bed and decreasing of the groundwater levels were observed (Trninić and Bošnjak 2009).

2.2 Sampling and sample preparation

TIMS was initially designed for small catchments where the sampler can be anchored by sinking the attached steel uprights directly in the stream bed. The high and fluctuating water level of the Sava River, along with its steep river banks, makes such a positioning difficult, if not impossible. The sampler was therefore hung from a boat permanently moored at the river bank. To maintain the stream-parallel position, TIMS was tied at its front and hind side with ropes bound to two neighboring deck bollards and, burdened with heavy weight to facilitate sinking, sunk below the water surface. Considering the similar particle size distribution (PSD) of the suspended load in the river surface cross-section (Walling et al. 2000), such positioning of TIMS should enable preferential accumulation of fine-grained fraction.

Sampling was performed over a nearly 1-year period, i.e., TIMS was immersed in the river for about a month in (1) August 2014, (2) October 2014, (3) February 2015, and (4) May 2015.

The PSD of the SPM accumulated in TIMS was determined immediately after retrieval, whereas the rest of the material was freeze-dried (FreeZone 2.5; Labconco, USA). Additionally, portions of dry samples intended for further analyses were subjected to different pretreatments. A part of dried SPM was treated with the H_2O_2 for the assessment of particle flocculation. Some of the collected material was ground to a fine powder using a ball-mill (Pulverisette 7; Fritsch, Germany) for the determination of mineral composition and metal analysis.

2.3 Analyses

The PSD was determined using a Beckman Coulter particle size analyzer (LS 13320; Beckman Coulter Inc.). The PSD was calculated by the proprietary software using the Mie theory of light scattering (optical parameters—refractive index = 1.53; absorption index = 0.1). The PSD was determined for native SPM samples and samples treated with the hydrogen peroxide.

Mineral composition of the samples was determined by X-ray powder diffraction method using a Philips X-Pert MPD diffractometer (40 kV, 40 mA, range scanned $4-63^\circ 2\theta$). For clay mineral identification, the samples were air-dried,

saturated by ethylene glycol, and heated for half an hour at 400 and 550 °C. Mineral phases were identified using a X'Pert High score software, while mineral percentages were modeled with the Rietveld method using the Profex software (Döbelin and Kleeberg 2015). Carbonate fraction was additionally determined by the volumetric method using a Scheibler apparatus (ISO: 10693 2014). Morphological characteristics of the SPM were inspected by scanning electron microscopy (JSM 7000F; Jeol Ltd). Total organic carbon (TOC) content was determined using a Shimadzu SSM-5000A connected to a TOC-VCPh analyzer, using the high-temperature (680 °C) catalytic (Pt/silica) oxidation method with IR detection of CO₂ and calibrated with D(+) glucose (Merck, Germany).

Microwave digestion system Multiwave 3000 (Anton Paar) was used for digestion of the SPM samples by a two-step digestion procedure (4 ml HNO₃ + 1 ml HCl + 1 ml HF; II—6 ml 40 g l⁻¹ H₃BO₃). After digestion, the solution was transferred to a volumetric flask and diluted with Milli-Q water to 100 mL. Elemental analysis was performed using a high-resolution inductively coupled plasma mass spectrometer (HR ICPMS) Element 2 (Thermo Finnigan, Bremen, Germany). Quality control of analytical procedure was performed by simultaneous analysis of blank and certified reference material (NCS DC 73309 or GBW 07311; China National Analysis Center for Iron and Steel, Beijing, China). The accuracy of the results was 5–10%, depending on the metal measured. Details of the method are described in Fiket et al. (2017).

Pearson's correlation analysis was used to evaluate the relationships between different variables using Statistica for Windows ver. 7.0 (StatSoft Inc., USA).

The hydrological data were obtained from the Meteorological and Hydrological Service of Croatia. Discharge measurements were performed by conventional current meter method at the Zagreb gauging station. The SPM concentration was measured daily by filtration of surface water samples taken in the middle of the river course.

3 Results

3.1 The Sava River hydrological characteristics

The Sava River channel is approximately 100 m wide and up to 6 m deep at the sampling location (Gilja et al. 2011). Significant water level fluctuations are quite frequent, reaching at times more than 4 m day⁻¹.

The spring and summer of 2014 were hot and rainy and high precipitation period extended into autumn. Due to the extreme conditions, the Sava River overflowed its banks several times resulting in catastrophic floods in the lower reaches of the river. High water levels were also observed during the sampling periods in August and October 2014 with the

average daily discharge (Q_{ad}) ranging from 140 to 990 m³ s⁻¹ and from 150 to 1070 m³ s⁻¹, respectively (Fig. 2). In 2015, the Sava River resumed more moderate hydrological conditions. In February 2015, Q_{ad} ranged from 200 to 460 m³ s⁻¹, while in May 2015 values were between 115 and 220 m³ s⁻¹ (Fig. 2). The concentrations of the SPM (g m⁻³) were in concordance with the discharge fluctuations. The high content of the SPM was observed in summer and autumn of 2014, with the highest value of 200 g m⁻³ measured in October that year (Fig. 2).

The physicochemical conditions in the river water and water collected inside TIMS were in concordance with sampling periods (Table 1). The average temperature of the river ranged from 6.3 °C in February to 18.4 °C in August. The pH values of the river water, measured at the end of each sampling period, varied between 7.47 (October 2014) and 8.06 (May 2015). The pH of the TIMS water samples was somewhat higher ranging from 7.68 (October 2014) to 8.33 (May 2015).

3.2 SPM characteristics

3.2.1 Particle size

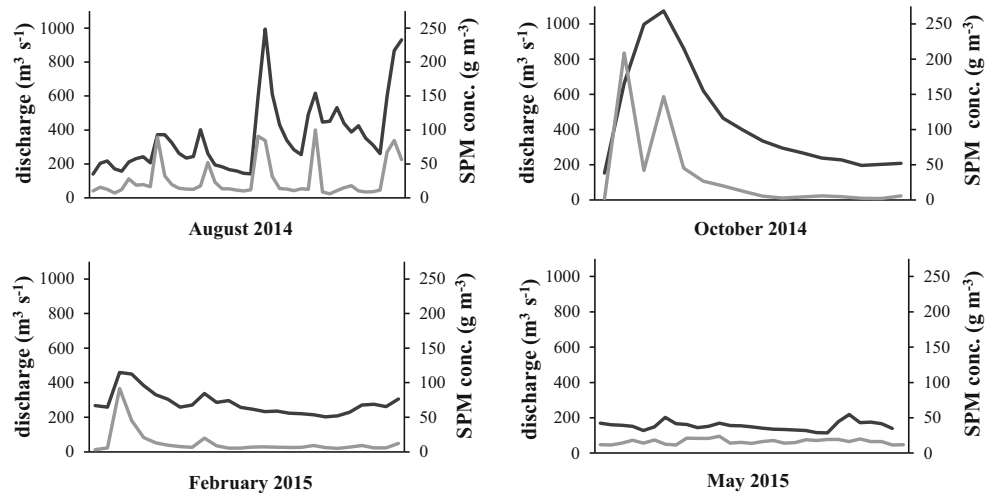
The SPM samples collected by TIMS predominantly contained silt-sized particles regardless of the sampling period (Fig. 3, Table 2). Samples 1 (August 2014) and 2 (October 2014) had similar particle size distribution; silt fraction was prevailing (75.2 and 75.3%), followed by sand (18.6 and 17.6%) and clay (6.2 and 7.1%). The M_z of these samples was 41.8 and 39.3 μm, respectively. Sample 3 (February 2015) differed only slightly. It consisted of 78.0% silt, 10.2% sand, and 11.8% clay fraction with the M_z of 28.0 μm. Only sample 4 (May 2015) consisted of nearly equal proportions of silt and sand, 44.7 and 53.4%, respectively, with a minute contribution of clay (1.9%). The mean particle size of the sample (M_z) was 124.0 μm, but the particle size distribution of this sample changed significantly after the organic matter removal.

Chemical dispersion of all four SPM samples (H₂O₂ treatment) induced the increase of clay fraction content, and also the significant increase of silt content in sample 4 (from 44.7 to 74.9%). The mean particle size of samples after the treatment was between 12.3 and 22.1 μm; the lowest M_z (12.3 μm) was measured in sample 4.

3.2.2 Mineral composition and morphological characteristics

The XRD analysis of the SPM revealed the similar mineralogical composition of all samples (Table 3). In samples 1–3 (August 2014, October 2014, and February 2015), dominant minerals were quartz and muscovite/illite. Calcite and dolomite followed, while kaolinite and feldspar were present as minor mineral phases. In sample 2, chlorite was also detected

Fig. 2 Water discharge (—) and suspended particulate matter (---) concentrations during sampling campaigns (data from Meteorological and Hydrological Service)



as a minor mineral, whereas in sample 3 vermiculite was found in traces. Mineralogical composition of sample 4 (May 2015) contained significantly different ratios of present minerals. The dominant mineral was calcite (53.2%), while muscovite/illite and quartz contents were lower (14.4 and 13.5%, respectively). Minor components were kaolinite (7.9%), dolomite (7.5%), and feldspar (3.4%). The volumetric assessment of CaCO_3 was in good agreement with the results obtained by Rietveld method—the highest carbonate content of nearly 50% was measured in sample 4.

Morphological features of the SPM samples 1–3 (Fig. 4) revealed the predominance of flocculated material, composed predominantly of small inorganic particles, with occasional occurrence of larger grains and skeletal fragments of diatoms. Sample 4 differed significantly; the diatom fragments comprised a significant portion of this sample.

3.2.3 Multi-elemental composition

Concentrations of 28 elements in the SPM samples are given in Table S1 in the Electronic supplementary material. The highest concentrations of almost all elements were measured in February 2015. Most of the elements (Al, Fe, K, Mg, Na, As, Ba, Be, Co, Cr, Cs, Li, Ni, Rb, Sb, Ti, Tl, U, V, Zn) exhibit similar behavior, and higher concentrations were observed in the first three

sampling periods and the lowest in May 2015. The lowest concentrations of remaining elements (Bi, Cd, Cu, Mn, Mo, Pb, Sn, Sr) were measured in October 2014. The distributions of 15 selected elements (Al, Fe, As, Ba, Cd, Co, Cr, Cu, Mn, Ni, Pb, Sb, Ti, V, and Zn) are presented in Fig. 5 alongside the concentrations of the same elements determined in the Sava River SPM and sediments collected in the Zagreb area by Vidmar et al. (2016).

Pearson's correlation analysis was used to establish the relationships between different characteristics (sedimentological, geochemical, etc.) of the Sava River SPM. The statistically significant ($p \leq 0.05$) correlation coefficients for elements in the SPM are presented in Table 4. The complete Pearson correlation matrix for all measured elements is given in Table S2 in the Electronic supplementary material. The correlation coefficients between prevailing mineral phases and variables such as concentrations of trace elements, TOC content, the PSD, and water discharge are presented in Table 5.

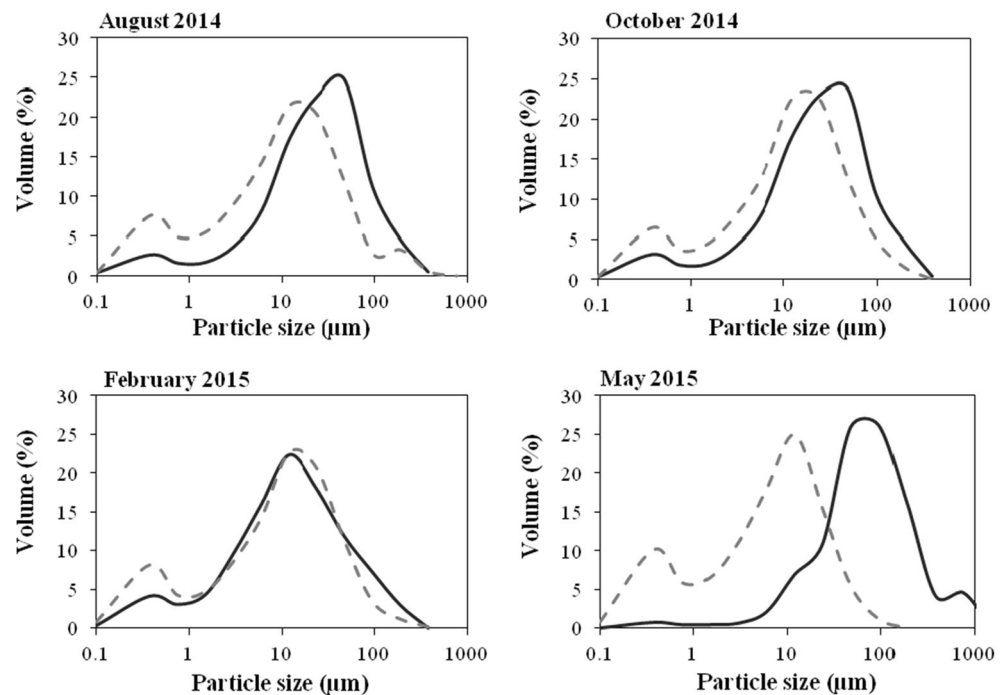
Due to a small number of samples ($N=4$), only r values equal or higher than 0.950 were found to be statistically significant at $p \leq 0.05$.

Positive correlations ($p \leq 0.05$) were found between Al and major elements Fe and K (Table 4). Positive correlations were also observed between at least one of these elements and trace elements As, Ba, Be, Co, Cr, Cs, Li, Ni, Rb, Sb, Ti, Tl, U, V, and Zn, with r values ranging from 0.950 ($p \leq 0.05$) to 0.997 ($p \leq 0.005$). Most of the trace elements were also significantly intercorrelated, especially Co and Cr ($r=0.999$), Co and Ni ($r=0.999$), Cr and Ni ($r=1.000$), and Rb and Be ($r=1.000$), with $p \leq 0.001$. Mg displayed a significant negative correlation with Bi ($r=-0.976$, $p \leq 0.05$) and Mn ($r=-0.993$, $p \leq 0.01$). Positive correlations were also observed between Mn and Bi ($r=0.968$, $p \leq 0.05$), Cd and Pb ($r=0.991$, $p \leq 0.01$), and Cu and Sr ($r=0.950$, $p \leq 0.05$).

Table 1 The average temperature during sampling periods and pH

Sampling		T (°C)	pH river	pH TMS
1	August 2014	18.4	8.05	—
2	October 2014	11.4	7.47	7.68
3	February 2015	6.3	7.63	7.98
4	May 2015	16.3	8.06	8.33

Fig. 3 Particle size distribution of SPM samples: (—) TIMS samples and (---) chemically dispersed TIMS samples



Quartz was found to be significantly positively correlated with U ($r = 0.983$, $p \leq 0.05$) and significantly negatively correlated with Bi ($r = -0.967$, $p \leq 0.05$) and calcite ($r = -0.961$, $p \leq 0.05$).

High correlation coefficients were found between muscovite/illite and the majority of major and trace elements (Table 5), although statistically significant correlations (p values ranging from 0.05 to 0.005) were found only with Fe, Be, Co, Cr, Ni, Rb, Sb, V, and Zn. A significant correlation between muscovite/illite and the clay fraction ($r = 0.955$, $p \leq 0.05$) was also found.

Contrary, calcite negatively correlated with most of the elements and the silt content but showed a positive correlation with the sand fraction ($r = 0.983$, $p \leq 0.05$).

For feldspar, a significant positive correlation was found between this mineral and Na concentration ($r = 0.978$, $p \leq 0.05$). Kaolinite was strongly correlated with Cu ($r = 0.998$, $p \leq 0.005$).

Besides the correlation with muscovite/illite, the clay fraction content was significantly positively correlated ($p \leq 0.05$) with Fe, As, Ba, Be, and V. Silt fraction content

positively correlated with Al, K, Ba, Li, Ti, Tl, and U (Table 5).

The Sava River discharge positively correlated with Mg concentrations ($r = 0.999$, $p \leq 0.001$) and negatively correlated with Mn ($r = -0.996$, $p \leq 0.005$) and Bi ($r = -0.969$, $p \leq 0.05$). Contrary, the TOC content negatively correlated with Mg concentrations ($r = -0.994$, $p \leq 0.01$) and also the discharge ($r = -0.997$, $p \leq 0.005$). An extremely strong, statistically significant, positive correlation was found between TOC and Mn ($r = 1.000$, $p \leq 0.001$), whereas TOC correlation with Bi was somewhat weaker ($r = 0.965$, $p \leq 0.05$).

4 Discussion

4.1 Hydrological characteristics and particle size distribution (PSD)

The increase of the SPM concentrations in the Sava River showed a good agreement with the higher water discharge

Table 2 Particle size distribution, mean size (M_z), and median size (d50) of the SPM collected by TIMS and chemically dispersed TIMS samples

Sampling period	TIMS					TIMS, chemically dispersed				
	Clay %	Silt %	Sand %	M_z (μm)	d50 (μm)	Clay %	Silt %	Sand %	M_z (μm)	d50 (μm)
1 August 2014	6.2	75.2	18.6	41.8	26.6	18.8	77.2	4.0	18.0	10.2
2 October 2014	7.1	75.3	17.6	39.3	25.1	14.0	79.3	6.7	22.1	13.4
3 February 2015	11.8	77.8	10.4	28.0	14.2	17.8	77.7	4.5	18.6	11.2
4 May 2015	1.9	44.7	53.4	124.0	72.1	23.5	74.9	1.6	12.3	7.5

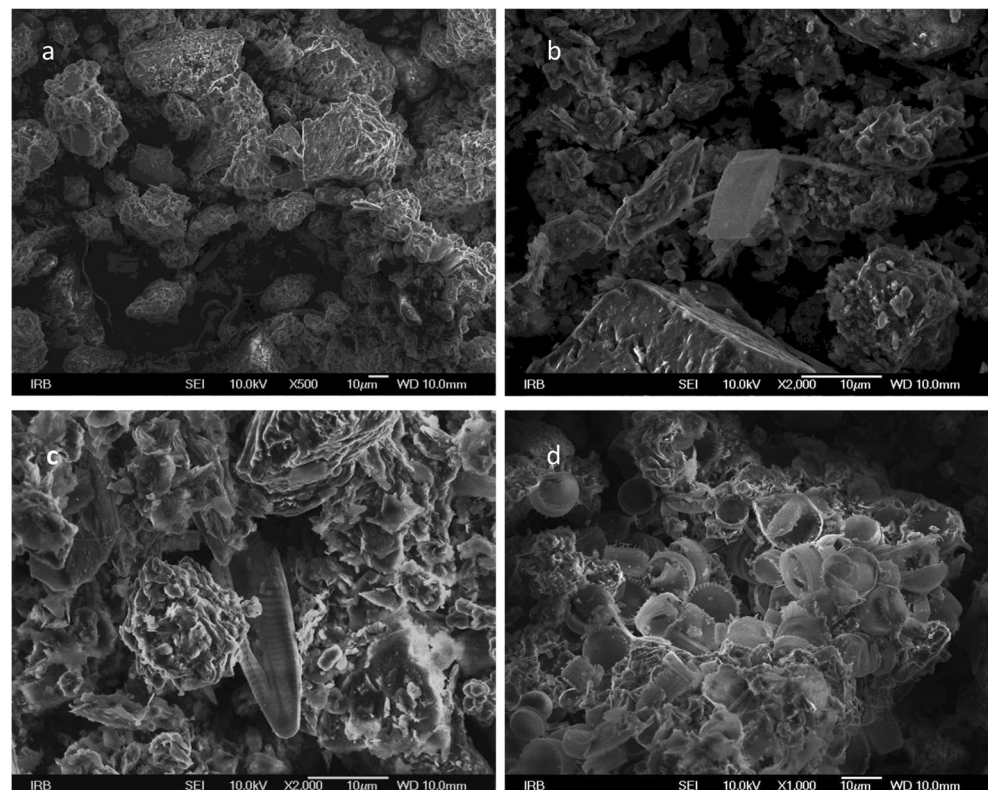
Table 3 Mineral composition calculated by Rietveld refinement, total organic carbon (TOC), and total calcium carbonate

% Component	August 2014	October 2014	February 2015	May 2015
Quartz	26.7	34.6	28.7	13.5
Muscovite/illite	24.7	20.5	32.3	14.5
Calcite	20.3	11.2	11.2	53.2
Dolomite	16.2	16.9	7.9	7.5
Kaolinite	8.2	4.7	13.3	7.9
Feldspar	3.9	5.7	6.1	3.4
Chlorite	—	6.3	—	—
Vermiculite	—	—	<1	—
TOC	3.4	2.0	4.6	6.1
Calcium carbonate	30.4	24.8	16.0	46.6

(Fig. 2). The PSD of TIMS collected samples was not significantly influenced by either the discharge or the SPM concentration (Table 5). The SPM of samples 1 to 3 (August 2014, October 2014, and February 2015) predominantly contained silt-sized particles (> 75%) (Fig. 3, Table 2). In the same periods, the SPM concentrations and water discharge differed significantly (Fig. 2). The SPM collected in May 2015 (sample 4) contained the coarsest material (Fig. 3, Table 2), which was at first attributed to the positioning of TIMS. The low discharge coincided with low SPM concentration (Fig. 2), i.e., with low input of fine-grained material. In addition, low discharge brought TIMS closer to the riverbed where coarser

material could have entered the sampler. However, the PSD results after H_2O_2 treatment disproved that conclusion (Fig. 3). The decrease of mean size and median after the treatment was most prominent in sample 4. Therefore, the cause for the observed PSD of sample 4 was believed to be due to flocculation processes inside TIMS promoted by high organic matter content (Table 2).

The dominance of composite particles in the riverine SPM, resulting from flocculation processes, was previously established in various catchments (Droppo and Ongley 1994; Droppo et al. 1997, 2005; Woodward and Walling 2007). According to the results presented here (Figs. 3

Fig. 4 SEM micrographs of TIMS samples: **a** August 2014, **b** October 2014, **c** February 2015, **d** May 2015

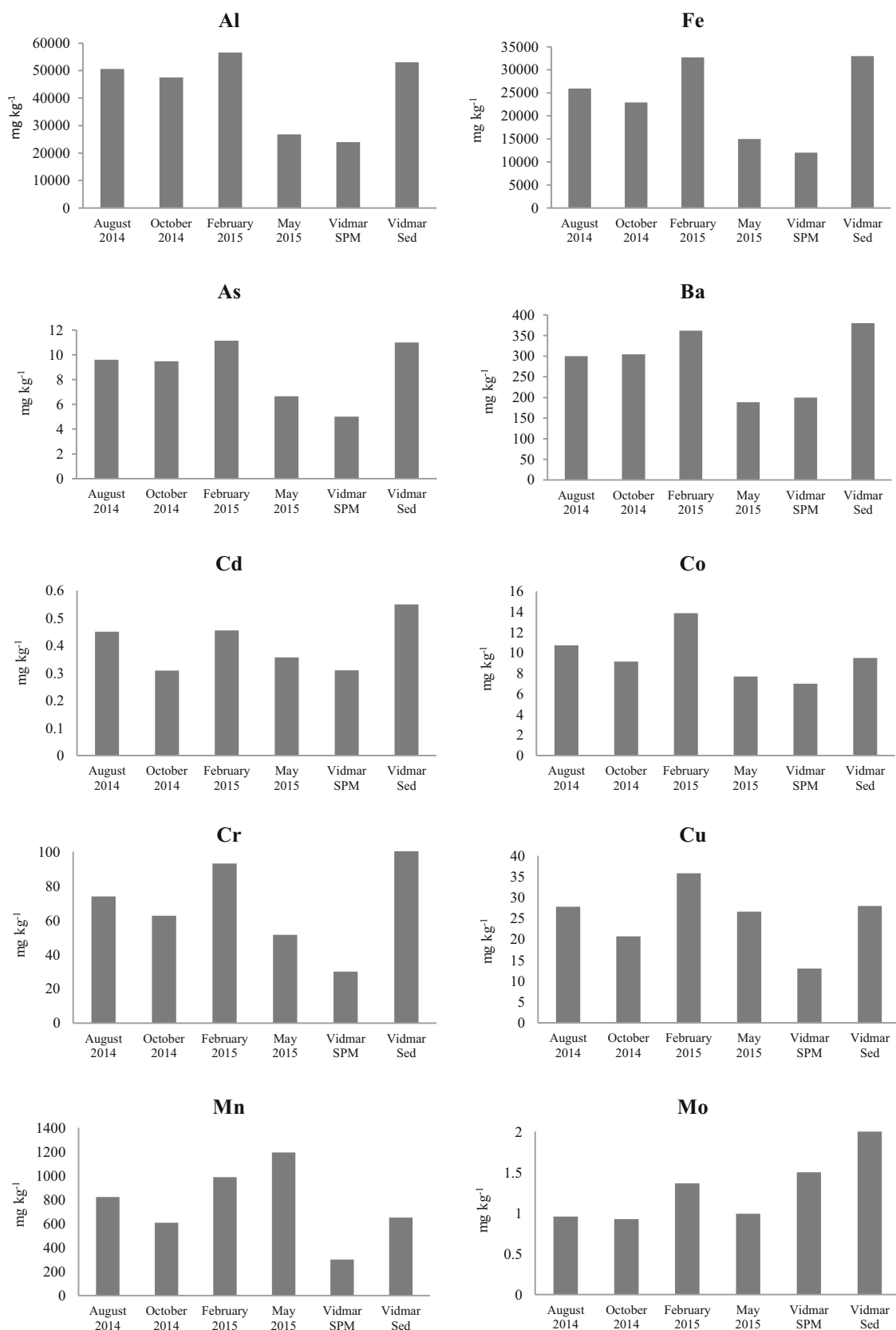


Fig. 5 Element concentration in TIMS samples of the Sava River compared to data of Vidmar et al. (2016)

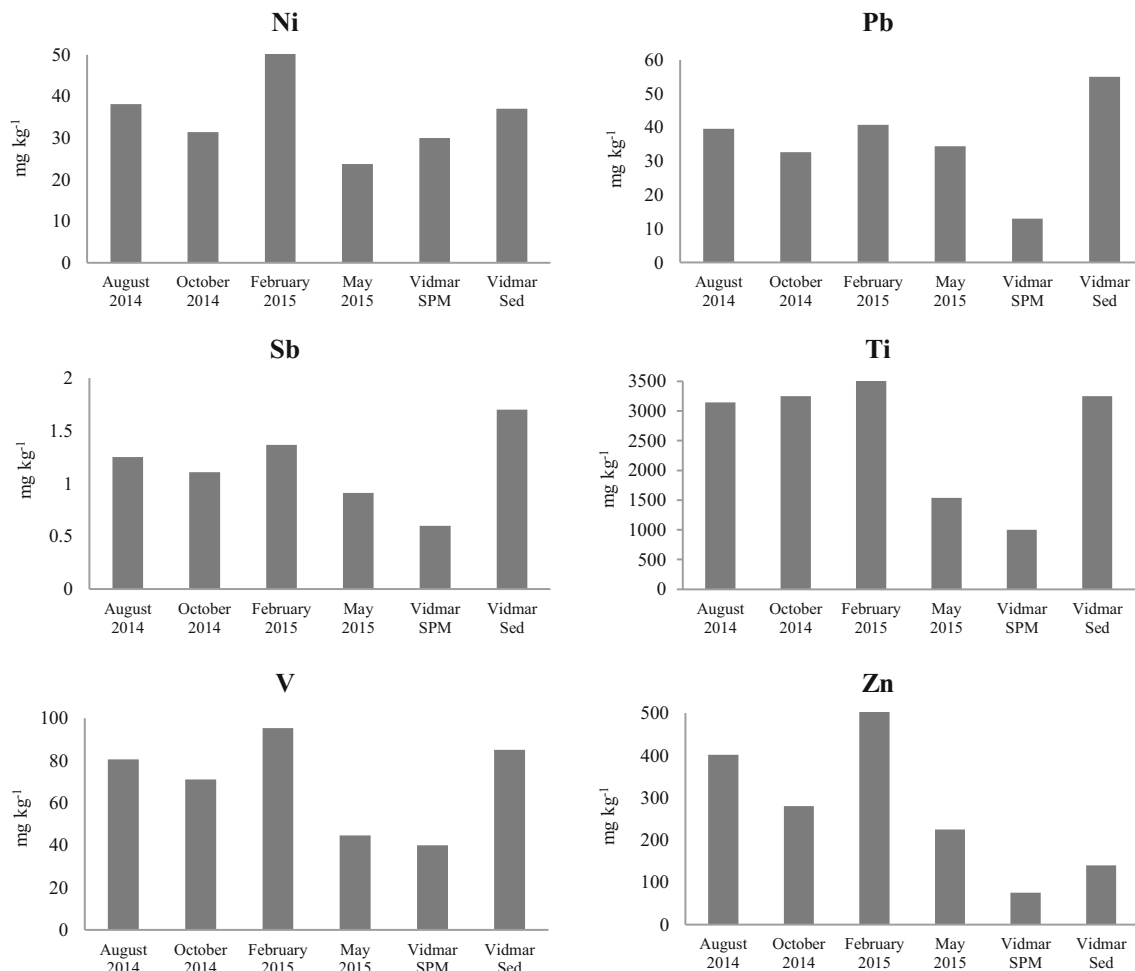


Fig. 5 (continued)

and 4; Table 2), the same processes can be confirmed in the Sava River. In addition, the flocculation was probably enhanced in TIMS due to SPM accumulation in a confined space with limited or no water movement.

4.2 Mineral composition and watershed lithology

The source of mineral components determined in the SPM samples can be traced back to the bedrock composition of the Sava River watershed and its tributaries. Quartz, muscovite/illite, feldspar, and kaolinite, found in all samples, probably derived from weathering of siliciclastic rocks along the Sava River watershed. These rocks were dominantly present in the catchments of the Savinja River and its tributaries Voglajna and Hudinja in Slovenia (Frančičković-Bilinski 2008; Szramek et al. 2011). Dolinar and Vrecl-Kojc (2010) specified muscovite/illite as a major mineral of the riverine suspended load upstream of our sampling location. A positive correlation established between muscovite/illite and the clay fraction indicates its presence as the main constituent of the fine-grained portion of the collected SPM. The source of

kaolinite can be traced to the soils deriving from Pleistocene fluvioglacial terraces, which comprise 15% of siliciclastic components (Vidic et al. 1991). Indeed, Štern and Förstner (1976) observed that kaolinite content in sediments increased downstream of Sava–Savinja confluence.

Carbonates, more specifically calcite and dolomite, also comprised a significant portion of the SPM samples (Table 3). The dolomite bedrock in the spring area of the Sava River is identified as the most probable source of dolomite. Intense rainfall periods, in summer and autumn 2014, were accompanied by high dolomite content in the suspended sediment load confirming the detrital character of this mineral.

The origin of calcite in the Sava River SPM was harder to determine. Taking into account that limestone bedrock occurs in many areas of the Sava River watershed, portion of calcite found in riverine suspended load is undeniably also detrital in origin. However, high content of calcite (53.2%) found in sample 4 (May 2015) arose some questions.

Calcite positively correlated with sand fraction content in native samples which suggests that high content of calcite found in the SPM collected in May 2015 could be due

Table 4 Statistically significant ($p \leq 0.05$) Pearson correlation coefficients for elemental concentrations in the Sava River SPM collected by TIMS ($N = 4$)

	Al	Fe	K	Mg	As	Ba	Be	Bi	Cd	Co	Cr	Cs	Cu	Li	Ni	Rb	Sb	Ti	Tl
Fe	0.957 ^d																		
K	0.972 ^d																		
As	0.989 ^d	0.979 ^d																	
Ba	0.986 ^d	0.967 ^d	0.956 ^d		0.998 ^b														
Be	0.995 ^b	0.982 ^d			0.995 ^b	0.989 ^d													
Bi				−0.976 ^d															
Co		0.971 ^d																	
Cr		0.980 ^d								0.999 ^a									
Cs	0.950 ^d						0.956 ^d												
Li	0.996 ^b		0.989 ^d		0.976 ^d	0.977 ^d	0.981 ^d												
Mn				−0.993 ^c				0.968 ^d											
Ni		0.981 ^d							0.991 ^c	0.999 ^a	1.000 ^a								
Pb																			
Rb	0.995 ^b	0.980 ^d			0.991 ^c	0.984 ^d	1.000 ^a					0.965 ^d		0.981 ^d					
Sb	0.958 ^d	0.988 ^d			0.960 ^d		0.979 ^d			0.952 ^d	0.967 ^d	0.981 ^d			0.964 ^d	0.982 ^d			
Sr													0.950 ^d						
Ti	0.984 ^d		0.997 ^b		0.967 ^d	0.975 ^d	0.963 ^d							0.994 ^c		0.961 ^d			
Tl	0.994 ^c	0.969 ^d			0.981 ^d	0.972 ^d	0.995 ^b					0.977 ^d		0.983 ^d		0.998 ^b	0.981 ^d	0.959 ^d	
U			0.972 ^d															0.954 ^d	
V	0.982 ^d	0.993 ^c			0.988 ^d	0.977 ^d	0.996 ^b				0.954 ^d	0.965 ^d		0.960 ^d	0.954 ^d	0.996 ^b	0.992 ^c		0.991 ^c
Zn		0.959 ^d								0.985 ^d	0.990 ^c				0.986 ^d		0.967 ^d		

Two-tailed probabilities. ^a $p \leq 0.001$; ^b $p \leq 0.005$; ^c $p \leq 0.01$; ^d $p \leq 0.05$

to the detrital input of coarser material. This hypothesis was unfortunately proven null. The H_2O_2 treatment of sample 4 significantly lowered the sand content in favor of clay and silt fractions indicating flocculation processes as the primary reason for the apparent coarser grain size (Table 2). It is possible that particularly low discharge in May 2015 (Fig. 2) influenced the mineral composition of sample 4. The reduced delivery of aluminosilicates and quartz, commonly originating from the Slovenian part of the Sava River watershed, could account for the atypically high amount of calcite in sample 4. Low discharge and low SPM concentrations were also observed in February 2015 (Fig. 2), but there was a surge in water discharge and suspended sediment load at the beginning of this sampling period. If most of the material was collected during this short event the similarities in mineralogical composition of the sample 3 with samples 1 and 2 are understandable.

The high content of calcite could also be attributed to the authigenic mineral precipitation processes induced by biological activity in the river. The evidence of algal control of calcite nucleation in the freshwater environment was found by Stabel (1986), the occurrence of biogenic calcite precipitation in lake sediments was also observed by Ivanić et al. (2017). Ollivier et al. (2011) assumed biogenic calcite precipitation processes in the River Rhône. The high TOC content (Table 3) and abundant algal remains (Fig. 4) in the riverine suspended load collected in May 2015 favor the possibility that biological activity induced the precipitation of calcite in the Sava River, but no definite conclusion can yet be reached. The similar problem concerning the detrital or biogenic origin of calcite in the SPM was also described in the Seine River by Roy et al. (1999). Additional sampling campaigns, targeting low river discharge and high primary production, are planned in the effort to determine the cause for higher calcite content in the Sava River suspended load.

Occasional occurrence of other minerals, i.e., vermiculite and chlorite, can be attributed to physical and chemical weathering processes (Setti et al. 2014). Chlorite was found in sample 2 (October 2014), in the period with the highest discharge, which suggests that the occurrence of this mineral is a consequence of the increased material input from the Sava River upper watershed (Milačič et al. 2017).

Vermiculite was present in traces only in sample 3 (February 2015). Its origin could be due to the chemical weathering of muscovite/illite during the pedogenesis along the Sava River banks (Vidic et al. 1991).

4.3 Trace element geochemistry

The major and trace elements geochemistry in the Sava River was examined based on their concentrations in the time-integrated SPM samples. The interrelations among elements

were determined and used to assess their mode of transport in the Sava River.

A positive correlation between major elements Al, Fe, K, and to some extent Na (Table 4 and Table S2 in the Electronic supplementary material) indicates their presence in the Sava River SPM as main constituents of the suspended load mineral component. These elements also predominantly correlate with clay and silt content (Table 5) indicating their presence in detrital aluminosilicate particles. Good correlation between mineral-forming and trace elements denoted mineral surfaces as preferred means of transport for trace elements.

Concentrations of Al and associated trace elements in different sampling periods did not correspond to the SPM concentrations or river discharge, but rather to the PSD and mineral composition of samples (Table 5). Such behavior emphasizes the input of the different type of material during high/low discharge periods. Milačič et al. (2017) have recently shown that during the high river discharge, as occurred in September 2014, contaminated river bank sediments and soils are washed into the Sava River, resulting in elevated levels of potentially toxic trace elements (PTEs) in the riverbed sediments. Ogrinc and Ščančar (2013) investigated the SPM in the Sava River in the spring and autumn 2006 at 33 locations along the river and its tributaries. The differences they found between two sampling points were at times greater than the differences between seasons, indicating that the metal concentrations could not be entirely attributed to the discharge regime and the river SPM concentrations.

The relationship between metal concentrations and water discharge is rather complex, but different materials are indeed brought into the river under different flow regimes. The significantly different mineral composition of sample 4 (May 2015) is a good example. Low river discharge in May 2015 is also reflected in the low SPM concentrations (Fig. 2) and the elemental composition of the collected sample (Table S1, Electronic supplementary material). Whereas the origin of the high content of calcite in the sample 4 is somewhat undetermined, its influence on the elemental composition is quite clear. Diluting effect of calcite on the elements of detrital origin and trace elements associated with them is revealed through the negative correlation between calcite and the majority of analyzed elements (Table 5).

In the study conducted by Vidmar et al. (2016), the concentrations of metals in the SPM were lower than in the Sava River sediments and predominantly lower than in any of the TIMS collected samples described in this study (Fig. 5). The discrepancy probably arises from different SPM sampling methods. The SPM investigated in this work was collected during an extended period, and possible variances in daily transported SPM composition may have been evened out during settling time inside TIMS. The SPM sampled by Vidmar et al. (2016) was a 1-day sample taken during the Sava River high discharge period (approximately

690 m³ s⁻¹). The SPM content is related to the water discharge, but inversely related to metal concentrations in particulate fraction, i.e., the increase of the water discharge is accompanied by an increment of detrital, metal-poor fraction of the SPM (Cobelo-Garcia and Prego 2004; Ollivier et al. 2011). Thus, the low metal concentrations in the Sava River SPM

found by Vidmar et al. (2016) may be explained by the timing of sampling.

On the other hand, the metal concentrations in the riverbed sediment, found by Vidmar et al. (2016), corresponded rather well to samples 1–3 (Fig. 5). Horowitz and Stephens (2008) and Smith and Owens (2014) pointed out that the bed

Table 5 Pearson correlation coefficients between different characteristics of the Sava River SPM collected by TIMS ($N = 4$)

	Quartz	Muscovite/ illite	Calcite	Dolomite	Feldspar	Kaolinite	Clay	Silt	Sand	Discharge	SPM	TOC
Al	0.822	<i>0.916</i>	<i>-0.946</i>	0.357	0.745	0.405	<i>0.927</i>	0.976^d	-0.989^d	0.638	0.135	-0.578
Fe	0.653	0.993^c	-0.837	0.076	0.735	0.651	0.970^d	0.873	<i>-0.913</i>	0.392	-0.158	-0.322
K	<i>0.931</i>	0.801	-0.992^c	0.522	0.776	0.186	0.864	0.999^a	-0.995^b	0.798	0.351	-0.751
Mg	<i>0.941</i>	0.311	-0.839	0.862	0.564	-0.412	0.452	0.809	-0.756	0.999^a	0.821	-0.994^c
Na	<i>0.907</i>	0.648	<i>-0.908</i>	0.276	0.978^d	0.120	0.839	0.823	-0.846	0.696	0.282	-0.668
As	0.794	<i>0.947</i>	<i>-0.931</i>	0.230	0.811	0.489	0.973^d	<i>0.946</i>	-0.974^d	0.562	0.030	-0.500
Ba	0.823	<i>0.930</i>	<i>-0.946</i>	0.249	0.838	0.452	0.972^d	0.953^d	-0.979^d	0.593	0.066	-0.533
Be	0.770	0.952^d	<i>-0.916</i>	0.260	0.748	0.497	0.951^d	<i>0.949</i>	-0.972^d	0.556	0.031	-0.492
Bi	-0.967^d	-0.327	0.858	-0.747	-0.700	0.374	-0.516	-0.794	0.757	-0.969^d	-0.760	0.965^d
Cd	-0.034	0.737	-0.229	-0.206	0.023	0.817	0.504	0.369	-0.405	-0.192	-0.544	0.262
Co	0.463	0.992^c	-0.687	-0.154	0.660	0.813	<i>0.936</i>	0.731	-0.789	0.160	-0.390	-0.086
Cr	0.491	0.997^b	-0.712	-0.103	0.655	0.789	<i>0.938</i>	0.759	-0.813	0.201	-0.349	-0.127
Cs	0.632	<i>0.924</i>	-0.806	0.296	0.521	0.525	0.840	0.889	-0.900	0.474	-0.006	-0.406
Cu	-0.153	0.729	-0.120	-0.634	0.225	0.998^b	0.575	0.190	-0.272	-0.453	-0.847	0.519
Li	0.866	0.874	-0.967^d	0.436	0.746	0.318	<i>0.900</i>	0.992^c	-0.997^b	0.707	0.226	-0.652
Mn	<i>-0.903</i>	-0.195	0.771	-0.888	-0.503	0.518	-0.349	-0.733	0.673	-0.996^b	-0.880	1.000^a
Mo	0.085	0.779	-0.312	-0.640	0.568	<i>0.933</i>	0.747	0.310	-0.405	-0.289	-0.751	0.349
Ni	0.500	0.997^b	-0.718	-0.109	0.674	0.786	<i>0.946</i>	0.761	-0.816	0.205	-0.348	-0.131
Pb	0.071	0.819	-0.337	-0.198	0.156	0.846	0.614	0.462	-0.503	-0.122	-0.529	0.195
Rb	0.762	0.952^d	<i>-0.910</i>	0.270	0.728	0.497	<i>0.943</i>	<i>0.949</i>	-0.970^d	0.555	0.033	-0.490
Sb	0.626	0.980^d	-0.816	0.149	0.633	0.629	<i>0.922</i>	0.877	-0.907	0.404	-0.124	-0.333
Sn	-0.021	0.390	-0.090	-0.766	0.582	0.633	0.488	-0.003	-0.096	-0.373	-0.663	0.397
Sr	-0.357	0.570	0.084	-0.599	-0.077	<i>0.928</i>	0.346	0.026	-0.091	-0.568	-0.848	0.629
Ti	<i>0.911</i>	0.840	-0.989^d	0.459	0.796	0.255	0.898	0.996^b	-0.999^a	0.753	0.282	-0.702
Tl	0.759	<i>0.938</i>	<i>-0.906</i>	0.316	0.686	0.471	<i>0.917</i>	0.953^d	-0.968^d	0.573	0.065	-0.508
U	0.983^d	0.639	-0.978^d	0.673	0.741	-0.047	0.743	0.967^d	<i>-0.944</i>	<i>0.915</i>	0.554	-0.883
V	0.710	0.974^d	-0.877	0.190	0.719	0.570	0.953^d	<i>0.918</i>	<i>-0.947</i>	0.482	-0.053	-0.414
Zn	0.421	0.983^d	-0.655	-0.091	0.545	0.805	0.884	0.727	-0.776	0.156	-0.372	-0.080
Quartz		0.558	-0.961^d	0.647	0.801	-0.128	0.712	<i>0.916</i>	-0.897	<i>0.926</i>	0.593	<i>-0.903</i>
Muscovite/illite			-0.765	-0.032	0.689	0.738	0.955^d	0.808	-0.857	0.278	-0.275	-0.205
Calcite				-0.507	-0.836	-0.140	-0.864	-0.984^d	0.983^d	-0.817	-0.378	0.775
Dolomite					0.068	-0.653	0.021	0.531	-0.441	0.882	<i>0.933</i>	-0.894
Feldspar						0.277	0.873	0.745	-0.788	0.530	0.085	-0.497
Kaolinite							0.601	0.199	-0.284	-0.444	-0.849	0.509
Clay								0.857	<i>-0.905</i>	0.416	-0.137	-0.354
Silt									-0.995^b	0.789	0.344	-0.741
Sand										-0.733	-0.255	0.680
Discharge											0.843	-0.997^b
SPM												-0.878

Two-tailed probabilities. Bolded r values: ^a $p \leq 0.001$; ^b $p \leq 0.005$; ^c $p \leq 0.01$; ^d $p \leq 0.05$. Italic r values: $p \leq 0.10$

sediment fraction < 63 μm is a suitable representative of suspended sediment load which was confirmed by the results of this study.

4.3.1 Enrichment factor analysis

The enrichment factor (EF) analysis is often used in studies concerning the geochemical behavior of elements in rivers, either to determine anomalous metal concentrations of natural origin or to assess the anthropogenic influence on metals in suspended solids (Gaillardet et al. 1999; Meybeck et al. 2007; Viers et al. 2009; Chen et al. 2014). The EF is calculated by double normalization of the element concentration, with the average composition of the upper continental crust (UCC) used as the reference background value (Taylor and McLennan 1985; Hu and Gao 2008):

$$EF(X) = (X/Al)_{\text{sample}} / (X/Al)_{\text{UCC}},$$

where $EF(X)$ = enrichment factor of selected element, and X/Al = selected element concentration normalized to Al concentration. The basis for normalization to the UCC chemical composition is the premise that large river catchments incorporate different lithologies and as such can be approximated by the upper continental crust constitution (Gaillardet et al. 1999). Hence, this approach was chosen to analyze the geochemical data obtained in this study, more precisely to determine the origin and processes affecting trace elements concentrations in the Sava River SPM.

The EFs for 27 elements are presented in Fig. 6, arranged along the x -axis as a function of the increasing EF value. In literature, several criteria were suggested to assess the sources of trace elements in the SPM and sediments based on their EF values. The consensus is that calculated ratios close to 1 indicate that studied element concentration can be explained by its terrigenous origin. In the riverine SPM, the EF values between 0.5 and 1.5 suggest the crustal origin of studied elements, and only $EF > 1.5$ indicates that a portion of trace element load is

probably derived from alternate sources (Zhang and Liu 2002).

In the Sava River SPM, the EF values of Na, Sr, K, Ba, Be, Rb, Tl, U, and Fe indicate their solely terrigenous origin. Na, Sr, K, and Ba showed $EF < 1$, with Na even slightly depleted due to its soluble character. The enrichment of these elements is commonly reported in the dissolved phase (Viers et al. 2009; Ollivier et al. 2011; Chen et al. 2014). Be, Rb, Tl, U, and Fe showed EF close to 1 with little variations.

In the Sava River suspended load, even Ti, Mn, Sn, Co, Mo, V, Cs, Mg, and Li can be considered predominantly geogenic in origin. Specifically, Sutherland (2000) suggested five contamination categories based on the EF values:

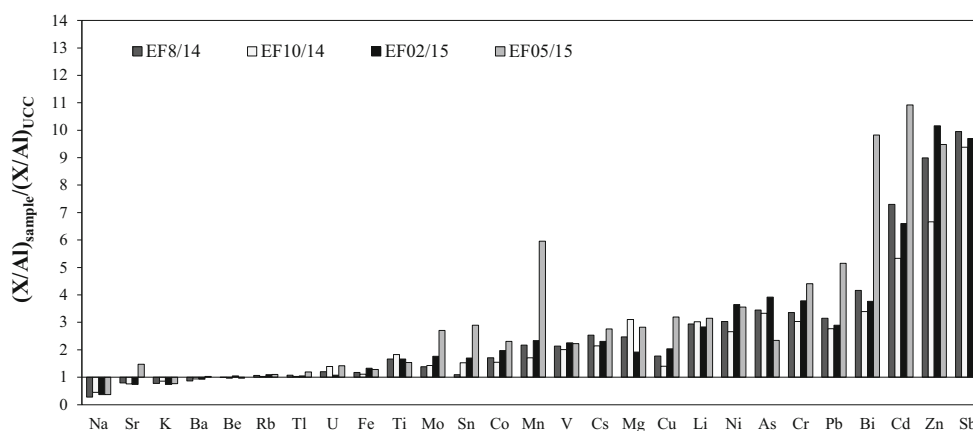
- EF < 2 minimal enrichment suggesting no or minimal pollution,
- EF = 2–5 moderate enrichment and pollution,
- EF = 5–20 significant enrichment and pollution,
- EF = 20–40 very high enrichment and pollution,
- EF > 40 enrichment indicating an extreme pollution signal.

In the analyzed SPM samples, Ti, Mo, Sn, and Co all showed $EF < 2$, except the EF values for Mo, Sn, and Co in sample 4 (May 2015) whose notably different mineralogical and geochemical composition was already discussed in previous sections.

The EFs between 2 and 3 were obtained for Mn, V, Cs, Mg, and Li, but their enrichment in the SPM could be of natural origin. Indeed, the abundance of Li in clay minerals was observed in the Sava River alluvial sediments, while V originates from Würm terraces (Šajin and Gosar 2014). It is probable that concentrations of other elements from this group also reflect regional lithology. Cu also displayed the EF mostly below 3 indicating only moderate enrichment of the SPM with this element despite its predominately anthropogenic origin.

The highest EF values (between 3 and 14) were obtained for Ni, As, Cr, Pb, Bi, Cd, Zn, and Sb, indicating pollution of

Fig. 6 Enrichment factors for 27 elements (concentrations normalized to Al) versus upper continental crust (UCC) (Taylor and McLennan 1985; Hu and Gao 2008)



the Sava River SPM with these elements during all sampling periods. Several authors (Štern and Förstner 1976; Kotnik et al. 2003; Frančišković-Bilinski 2008) detected the increased content of Cd, Cr, Cu, Ni, Pb, and Zn in sediment from the Slovenian part of the Sava River and associated the observed contamination with the metallurgical and mining activities in Slovenia. The anthropogenic input of Bi, Pb, Sb, and Zn into the environment could be the result of mining and smelting of galena and sphalerite, primary carriers of the mentioned trace metals. Pollution with Ni and Cr may also be related to the metal industry in Jesenice (Vidmar et al. 2016). Oreščanin et al. (2004) deduced that anthropogenic input of Cu, Zn, and Pb arises from fertilizing activities occurring in watersheds of the Sava River tributaries, the Krka and the Krapina Rivers.

It was recently shown (Milačič et al. 2017) that under high flood conditions of the Sava River, sediment pollution with ecotoxic elements may even pose an ecological risk. Therefore, the EF analysis of geochemical data collected in this study revealed that current environmental conditions of the Sava River are in concordance with previously reported moderate anthropogenic pressures on this aquatic ecosystem.

5 Conclusions

In this study, TIMS was used for the SPM sampling in the Sava River. Sufficient amount of the SPM was collected in a predetermined time span (1 month), during both high and low discharge periods, which enabled a considerable number of analyses to be conducted.

The differences in the PSD of the SPM samples, collected in different sampling periods, were not caused by the input of differently sized particulate material but rather the flocculation processes inside TIMS. The mineralogical composition of the Sava River SPM during first three sampling campaigns (August 2014, October 2014, and February 2015) was similar. Quartz and feldspars were present in silt fraction indicating their detrital origin, and the close association of quartz, muscovite/illite, kaolinite, and feldspar confirms the Sava River upper watershed as their common source.

The different ratios of present mineral phases and unusually high content of calcite in May 2015 sample indicate the input of the different type of material during low river discharges. However, the origin of calcite remains somewhat unclear. The close association of calcite with TOC and the presence of algal remains in TIMS collected SPM suggest the possibility of biogenic calcite precipitation and question its solely detrital origin.

Geochemical analyses of material collected by TIMS revealed that multi-elemental composition of the SPM is mainly governed by its mineralogical characteristics, e.g., muscovite/illite corresponded well with clay fraction and the majority of the trace elements thus confirming their preferential

adsorption to fine-grained clay mineral particle surfaces and associated transport in the Sava River suspended load. The analysis of collected geochemical data also indicated the input of material from different sources during high/low discharge periods and significant anthropogenic influence on the concentration of some ecotoxic elements (As, Bi, Cd, Cr, Ni, Pb, Sb, Zn).

Some issues were opened during this investigation; it appears that the physicochemical conditions inside the sampler invoke some reactions. Comparison of the SPM composition in this study with literature data shows better agreement with sediments than with the suspended material. It is possible that variances in daily transported suspended load composition evened out during prolonged sampling by TIMS. Further investigations on the subject are in progress.

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